The Report Committee for Hayrettin Aygol

Certifies that this is the approved version of the following report:

Foam Assisted Surfactant-Gas Flooding in Naturally Fractured Carbonate Reservoirs

Approved by Committee:

Kamy Sepehrnoori, Supervisor

Hamid Reza Lashgari

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Foam Assisted Surfactant-Gas Flooding in Naturally Fractured Carbonate Reservoirs

by

Hayrettin Aygol

Report

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Dedication

to
my hometown
HASANKEYF

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Abstract

Foam Assisted Surfactant-Gas Flooding in Naturally Fractured Carbonate Reservoirs

Hayrettin Aygol, M.S.E

The University of Texas at Austin, 2017

Supervisor: Kamy Sepehrnoori

In naturally fractured reservoirs, water flood performance and efficiency for oil recovery is usually limited by capillary forces. Wettability and interfacial tension (IFT) between oil and water phases are essential factors that limit the potential for oil production in naturally fractured reservoirs. The permeability of such reservoirs is in range of 1~20 md (majority of carbonate reservoirs) with the matrix wettability preferentially oil-wet to mixed-wet. Hence, water and/or gas flood performances are not efficient due to the tendency of water or gas flow through fractures. Surfactants are used to reduce IFT between oil and water, alter the wettability of matrix to proficiently water-wet, and generate in-situ foam as a drive and for mobility control. Spontaneous imbibition between the fractures and the matrix is achieved by both wettability alteration and ultra-low interfacial tensions.

Experimental studies show that co-injection or alternate injection of surfactant solution and gas are very promising to mobilize and solubilize the remaining oil. In this study, we overview to provide a technical background and review the literature extensively in order to understand surfactant flooding and foam performance in porous media. Results show that surfactants are induced to matrix through fractures not only by spontaneous imbibition, but also by foam that diverts surfactant solutions into low permeability matrix. The finding results by several authors in lab-scale indicate that surfactant type, foam properties, capillary pressure properties corresponding to different wetting states, and oil-water interfacial tension are crucial factors that significantly impact the efficiency of such processes.

In general, summary of this work shows that foam plays a dominant role as a drive to displace the oil in matrix when capillary forces are not strong to retain the oil in presence of surfactants. Although there is very restricted work that claim foam efficiency in presence of oil, mobilized oils are displaced and moved toward fractures as pure oil bank (oil phase). Some laboratory measurements and simulation study reveal with both core and reservoir scales that such process provides great sweep efficiency and recover a significant amount of remaining oil from the matrix to fracture.

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Chapter 1: INTRODUCTION

Oil recovery from a reservoir can be divided into three categories: primary, secondary, and tertiary, which is also known as Enhanced Oil Recovery. Primary recovery is driven by using natural reservoir energy (utilizing natural drive mechanisms, such as; rock and fluid expansion, solution-gas drive, gas cap drive, and gravity drainage) and artificial lift techniques (Green and Willhite, 1998). Generally, primary production is followed by the secondary recovery techniques. Secondary production refers to the injection of an external fluid such as water or/and gas for pressure maintenance to drive oil from the reservoir (Sheng, 2010). Water flooding is the main secondary recovery technique to maintain enough reservoir pressure to drive oil after primary production. However, it is not effective in naturally fractured carbonate reservoirs because water flows preferentially in the fractures and negative capillary pressure keeps water from entering the matrix, which leads to a high residual oil saturation (Delshad *et al*., 2006; Gupta and Mohanty, 2008; Li *et al*., 2012). It is estimated that a recovery of 35-50 % original oil in place (OOIP) can be achieved by combined primary and secondary production (Shah, 1981) and high amount of residual oil is left behind after these recovery techniques (Farouq-Ali and Stahl, 1970). Tertiary recovery follows the secondary production through the injection of fluids, such as; chemicals (surfactant solutions and polymers), miscible gases, steam, or the use of thermal energy to displace the residual oil and enhance the oil recovery (Sheng, 2010).

The overall displacement efficiency can be expressed as the product of microscopic and volumetric displacement efficiencies ($E = E_D E_v$). Overall efficiency (E) is the ratio of oil recovered by EOR process and oil present before the process (OOIP). Microscopic displacement efficiency (E_D) measures the effectiveness of the displacing fluid in mobilizing the oil at the local pore-level where displacing fluid contacts the oil whereas the volumetric displacement efficiency (E_v) measures the effectiveness of displacing fluids sweeping out the reservoir in a volumetric sense. Microscopic displacement efficiency (E_D) can be expressed as follows:

$$E_D = \frac{S_{oi} - S_{or}}{S_{oi}},$$

where S_{oi} is the initial oil saturation, and S_{or} is the residual oil saturation. Volumetric displacement efficiency (E_v) is the product of areal and vertical sweep efficiencies where the areal sweep efficiency is the fractional area of the pattern that is swept by the displacing fluid (Craig, 1971; Lake *et al*., 2014).

There are three major factors that affect the remaining oil saturation in a reservoir. The first factor is the capillary number ($N_c = \frac{v\mu}{\sigma cos\theta}$), where v is the superficial velocity, μ is the displacing fluid viscosity, σ is the interfacial tension (IFT), and θ is the contact angle. The capillary number affects the microscopic pore-level displacement efficiency. The second factor is the mobility ratio ($M = \lambda_D / \lambda_d$), defined as the ratio of mobility behind and ahead of a displacing front (Lake, 1989) where λ_D is the mobility of the

displacing fluid and λ_d is the mobility of the displaced fluid. In the previous equation, mobility of displaced fluid can be defined by:

$$\lambda_d = {}^{k_{rd}}/_{\mu_d},$$

where k_{rd} is the relative permeability, and μ_d is the viscosity of the displaced fluid.

The mobility ratio affects the volumetric displacement efficiency (Suffridge *et al*., 1989). At large mobility ratio, displacing fluid tends to bypass oil, resulting in poor oil recovery. High sweep efficiency can be achieved when mobility ratio is less than one ($M < 1$), but small mobility ratio means low injection rate. Thus, a practical mobility ratio is a compromise between mobility control and injection rate (Green and Willhite, 1998). Mobility can be controlled by adding polymer and foam. Reservoir heterogeneity is the third major factor that can influence the residual oil saturation. Reservoirs can contain impermeable layers and heterogeneous porosity/permeability distributions that notably affect the fluid flow path and distribution (Liu *et al*., 2002).

In this report several questions are going to answered properly in research challenges stand points as the following:

How can the microscopic displacement efficiency be improved? Residual oil remains trapped in the reservoir because of the pore structure of porous media, the wettability of the rock, and the capillary forces (Van Lingen *et al*., 1996). Capillary and viscous forces govern trapping of a phase and mobilization of fluids in porous media and thereby microscopic displacement efficiency. Capillary forces are proportional to the interfacial tension between the oil and the displacing fluid, so the trapped oil can be

mobilized by using miscible fluids or reducing the interfacial tension between the displacing fluid and the trapped oil to ultra-low values (Yu *et al*., 2008; Gupta and Mohanty, 2008)

How can the volumetric displacement efficiency be improved? The reasons for poor volumetric sweep efficiency are usually reservoir heterogeneities, gravity segregation and viscous fingering (Lescure and Claridge, 1986). Viscous fingering is caused by an unfavorable mobility ratio. It is possible to change the mobility ratio by either decreasing the mobility of the displacing fluid or by increasing the mobility of the displaced oil (Tripathi and Mohanty, 2007). Water-soluble polymers reduce water mobility in water floods.

The residual oil of water flooding is a result of high capillary force of water, competition between capillary and viscous forces (where strong capillary forces keep the residual oil immobile), and reservoir heterogeneities (Graue *et al*., 1998; Delshad *et al*., 2006). Thereby, Enhanced Oil Recovery methods are the only way to recover that residual oil in the reservoir. EOR applications can be classified into three categories as thermal, gas, and chemical methods (Lake, 1989).

Thermal methods are important recovery processes in heavy oil reservoirs (Osterloh and Jones, 2003). It is most commonly applied to heavy and medium-heavy crude oil reservoirs within formations of darcy-type permeability (Lake 1989; Green and Willhite 1998). Reservoirs have high remaining oil saturation. Thermal recovery includes steam flooding, hot-water injection, in-situ combustion, and electrical heating. Thermal processes rely mainly on the injection of thermal energy or the in-situ generation of heat

to improve oil recovery (Willman *et al*., 1961; Butler *et al*., 1981). Alteration of oil viscosity and achievement of favorable conditions such as thermal expansion or swelling of the oil are the primary mechanisms leading to improved oil recovery in thermal methods (Nasr and Ayodele, 2005; Lashgari, 2014). For instance, steam injection can reduce the viscosity of the heavy viscous oil, such that the flow resistance of oil through the reservoir is reduced and thus increase oil displacement. In addition to permeability, common limitations include formation depth, mineralogy, thickness, crude viscosity, heterogeneity, and oil saturation (Bogdanov *et al*., 2011; McGee *et al*., 1999). Thermal enhanced recovery processes cannot be applied to deep oil wells. Reservoir depth is the most crucial factor that influences the thermal recovery processes, especially for steam injection, due to wellbore heat losses (Beattie *et al*., 1991). Moreover, porosity should be high enough to diminish heat losses in the reservoir rock (Taghavifar *et al*., 2014; Ozdingis, 2016).

Gas injection is another recovery method applied to the reservoirs with a wide range of permeability, although application in tighter reservoirs of 5-20 md is most common. Hydrocarbon gases, carbon dioxide (CO_2), nitrogen (N_2), and flue gases are example of the gases used in gas injection processes where the recovery efficiency significantly depends on the miscibility (Green and Willhite 1998; Thomas, 2008). This method is also known as miscible flooding, because the displacing fluids should be miscible with the reservoir oil. Main mechanisms that miscible flooding contributes to improve oil recovery are (Taber *et al*., 1997):

- Vaporization of the light components of oil and miscibility generation if the pressure is high enough (minimum miscibility pressure)
- Increase in the volume of oil (oil swelling)
- Reduction in oil viscosity (CO_2 is more effective)

Availability of sufficient gas supply with desired composition is the most common limitation for the miscible gas injection method. Other common limitations include formation depth & temperature (miscibility parameters), thickness, geometry, crude oil chemistry, permeability, and heterogeneity (Lake, 1989; Taber *et al*., 1997).

Chemical injection is an effective method in reducing residual oil saturation and it is considered as a promising EOR application in many fields (Liu *et al*., 2008). Chemical methods, such as; alkaline, polymer, surfactant flooding, and/or their various combinations, might overcome most of the disadvantages that mentioned in the thermal and gas injection methods (Hirasaki *et al*., 2008). In chemical flooding, chemicals are added to achieve one or more of the following effects:

- Interfacial tension reduction
- Wettability alteration
- Mobility control

In alkaline flooding, alkaline concentration in the injection water is low, and alkali react with certain components (e.g. organic acids) in the oil to generate surfactant in-situ. Reduction of IFT at the water-oil interface and alteration of wettability are the main recovery mechanisms for alkaline flooding process (Green and Willhite 1998; Taber *et al*., 1997)

In polymer flooding, high molecular weight polymers are added to injection water to control mobility of the aqueous phase (Shah, 2012). Polymer floods achieve volumetric sweep efficiency by increasing the viscosity of water and thus decrease the mobility of water (Taber *et al*., 1997). High-molecular weight water soluble polymers can increase the viscosity of the aqueous phase significantly at low concentrations, resulting in improved waterflooding performance with higher volumetric displacement efficiency (Needham and Doe, 1987).

On the other hand, some reservoir conditions are not favorable for the use of polymers. These conditions are indicated as the following (Srivastava *et al*., 2009):

- Very low permeability rocks, accordingly high molecular weight polymers can plug the pore throats. Using polymers with a lower molecular weight may increase the cost of process.
- In naturally fractured carbonate reservoirs which have low permeability, the use of polymer may result in the loss of permeability
- Reservoirs with high salinity and temperature conditions, many of the commercially available EOR polymers are unstable (Buchgraber *et al*., 2009)
- At high flow rate through chokes or perforations, some polymers can mechanically degrade due to high shear stress
- Unfavorable interactions of polymers with under some conditions

Surfactant flooding can reduce oil-water interfacial tension (IFT) and/or alter wettability and thereby increase oil recovery. However, the most serious limitations for surfactant flooding are its excessive cost and losses due to the adsorption to the

rock surface, phase partitioning and trapping, and precipitation in some hard brine cases (Kessel, 1989; Hirasaki *et al*., 2008; Tavassoli, 2014).

The system of combined surfactant/polymer injection is very expensive and chemicals loss in the porous medium can be severe. Relatively low-cost alkali can be added to promote IFT reduction and reduce surfactant adsorption. (Shah, 2012). Alkali/Surfactant/Polymer (ASP) flooding is considered as a promising chemical EOR method because it combines polymer, surfactant, alkali flooding advantages together and exhibit great performance in several laboratory investigations and field applications (Kazemi Nia *et al.,* 2014). In this flooding, low-cost alkali is used by reducing the amount of surfactant. However, such chemical EOR methods are likely restricted by the reservoir permeability and heterogeneity beside the high cost of chemicals (Olajire, 2014).

A promising cost-effective EOR process is to combine surfactant flooding with gas injection to generate foam. This method provides better mobility control and utilizes less chemicals (Suffridge *et al*., 1989). Foam can be generated by co-injection or alternate injection of gas and foaming agent (Vassenden *et al*., 1998). For improving sweep efficiency in chemical EOR process, foam can be an alternative to polymer as a mobility control agent by causing a reduction in gas mobility.

Mobility control is obtained in the foamed region since the permeability of gas in the foamed region is reduced significantly (Ali *et al*., 1985; Lee and Heller, 1990; Zhang *et al*., 2000). The efficiency of the foam is believed to be the result of the high apparent viscosity of the foam and its penetration into the high permeability layers

and/or fractures (Li *et al*., 2012). Moreover, foam can block and restrict the flow of undesired fluids; coning of gas & water in production wells (Green and Willhite, 1998). Also, the recovery mechanisms in foam flooding are related to the effectiveness in reducing interfacial forces that hold residual oil in place, and the capability of altering flow distribution and fluid conductivity (Zhang *et al*., 2000). As a result, it is important to understand foam performance in a foam assisted surfactant-gas flooding process.

1.1 REPORT OBJECTIVE

This report focuses on foam assisted surfactant flooding and mechanisms during gas and chemical injection process. The objectives are the following:

- Understand the effect of surfactant on the overall performance,
- Understand the effect of surfactant types on various performance properties and choose a proper surfactant,
- Examine the effect of wettability alteration for oil recovery,
- Understand the mechanisms behind the process,
- Present the concepts of foam flow and its behavior in porous media, and
- Combine the process with foam for mobility control.

1.2 REVIEW OF CHAPTERS

This report is divided in chapters with the following contents:

Chapter 1 introduces the concept of enhanced oil recovery and reviews existing recovery methods. Then, this chapter discusses the application of current EOR methods with their attributes and limitations. Chemical EOR is explained in great detail, besides the major factors manipulating the remaining oil saturation. Finally, the objective of this report is outlined followed by the review of chapters.

Chapter 2 provides a detailed technical background in order to understand foam assisted surfactant flooding. Basic background about surfactants is introduced and effects of different surfactant types on oil recovery are discussed. Foam generation mechanisms and fundamentals of foam flow in porous media are reviewed. Then, extensive literature was reviewed. Laboratory experiments and field applications are reviewed in the literature for surfactant and foam flooding. Wettability and wettability measurement methods in the literature are presented. Finally, Displacement mechanisms of surfactant flooding are explained.

Chapter 3 gives a summary, demonstrates conclusions of this report, and finishes with recommendations for future work.

Chapter 2: TECHNICAL BACKGROUND

The following chapter will mainly introduce basic background about surfactants, some principles of foam and its generation in porous media, wettability and its measurement methods, and displacement mechanisms during surfactant flooding.

2.1 SURFACTANTS

The surfactant term is a contraction of surface active agent. Surfactants are chemical substances that adsorb on or concentrate at surfaces or interfaces between phases. In their most common form, surfactants consist of a nonpolar (hydrocarbon chain) portion and a polar (ionic) portion. Surfactants are amphiphilic which means that they contain both hydrophilic and hydrophobic groups. The polar portion is usually called the head, and the hydrocarbon chain is often called the tail of the molecule (Holmberg *et al*., 2002).

Figure 2.1 is a simplified sketch of the surfactant molecule. The hydrophobic tail is the water-insoluble component while the hydrophilic head is the water-soluble component. In aqueous solution, the hydrocarbon portion interacts with water molecules very weakly. Water molecules try to extract hydrocarbon out of the water. Therefore, the tail is called hydrophobic. On the contrary, since the head (polar portion) interacts strongly with water, this portion of the surfactant is called hydrophilic (Figure 2.2). As shown in the figure, surfactant molecules (head and tail) tend to attack and form a layer at surfaces or between interfaces with the hydrophilic head residing in the water medium while the hydrophobic tail residing in the non-polar oil medium. Thus, surfactants

significantly alter the interfacial properties between two surfaces or interfaces (Rosen and Kunjappu, 2012).

Surfactants decrease the interfacial forces between two surfaces, reduce the surface tension, or interfacial tension (IFT) between two phases (Delshad *et al*., 2006; Gupta and Mohanty, 2008; Kalaei *et al*., 2013).

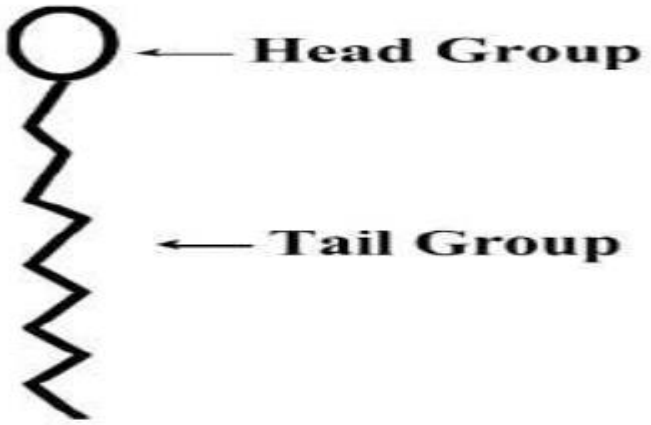


Figure 2-1 Structure of surfactant molecule (Tadros, 2005)

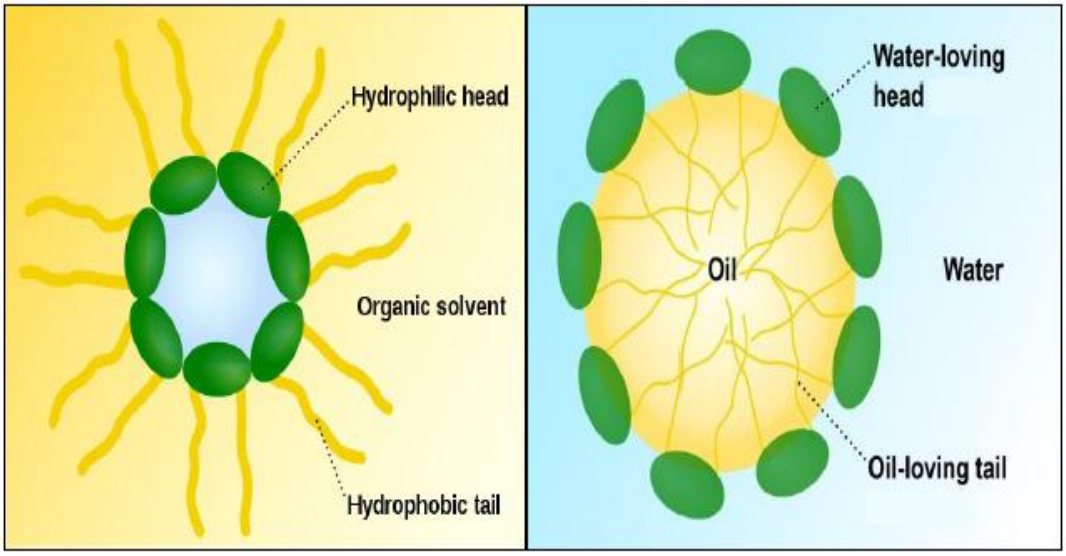


Figure 2-2 Surfactant chemical structure (Aman Zach, 2010)

2.2 SURFACTANT CLASSIFICATION

Surfactants are classified as anionic, cationic, nonionic, and zwitterionic (amphoteric) with respect to the ion charge of the surfactant head group.

2.2.1 Anionic Surfactants

Anionic surfactants have a negative charge on its head group. In aqueous solution, the molecule ionizes, and metal cation separated from the head group. Anionic surfactants have been most widely used in Enhanced Oil Recovery (EOR) applications. Because they have low adsorption on the rock matrix. Since they can be produced economically, they have a low cost on EOR processes. They are relatively stable. Sulfates, sulfonates, carboxylates, etc. are some examples of anionic surfactants (Holmberg *et al*., 2002).

2.2.2 Cationic Surfactants

These surfactants classified as cationic because of the negative charge on its polar head group. In aqueous solution, ionization occurs, and the head has a positive charge (cationic). Due to the high adsorption rate on the rock surface, cationic surfactants are rarely used in EOR applications. These surfactants are generally more expensive than anionic surfactants. Pyridinium, piperidinium, etc. are some examples of cationic surfactants (Holmberg *et al*., 2002; Rosen and Kunjappu, 2012).

2.2.3 Nonionic Surfactants

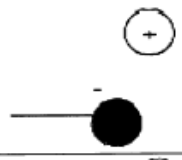
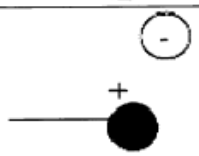
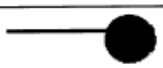
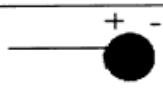
A nonionic surfactant does not have any charged group on its hydrophilic head. When it is dissolved in aqueous solution, ionization does not occur. The head group is larger than the tail group in this structure. Nonionic surfactants are mainly used as cosurfactants to improve phase behavior and increase solubility. Although they have high salinity

tolerance than anionic surfactants, nonionic surfactants cannot have a considerable influence on IFT reduction as well as anionic surfactants. Polyoxyethylene, alkanolamides are some examples (Rosen and Kunjappu, 2012).

2.2.4 Zwitterionic (Amphoteric) Surfactants

Zwitterionic surfactants have both positive and negative charges (opposite charge) on its head. They dissociate in water into cationic and anionic parts. These surfactants contain two or more of the other classes. Some common surfactants include sultaines, betaines, etc. Figure 2.3 shows types of surfactant structures. Table 2.1 exhibits the surfactant classification with their examples and structures (Holmberg *et al*., 2002; Rosen and Kunjappu, 2012).

Table 2-1 Classification of surfactants (Akstinat, 1981)

Class	Examples	Structures
Anionic: negatively charged head group	Sulfonates Sulfates Carboxylates Phosphates	
Cationic: positively charged head group	Quanternary ammonium organics, amines, pyridinum, imidazolinium, piperidinium, sulfonium compounds	
Non-ionic: molecule does not ionize	Alkyl-, Alkyl- aryl-, acyl-, acylamindo-, acyl- aminepolyglycol polyol ethers Alkanolamides	
Zwitterionic: with two or more of the other classes	Aminocarboxylic acids, Betaine surfactants	

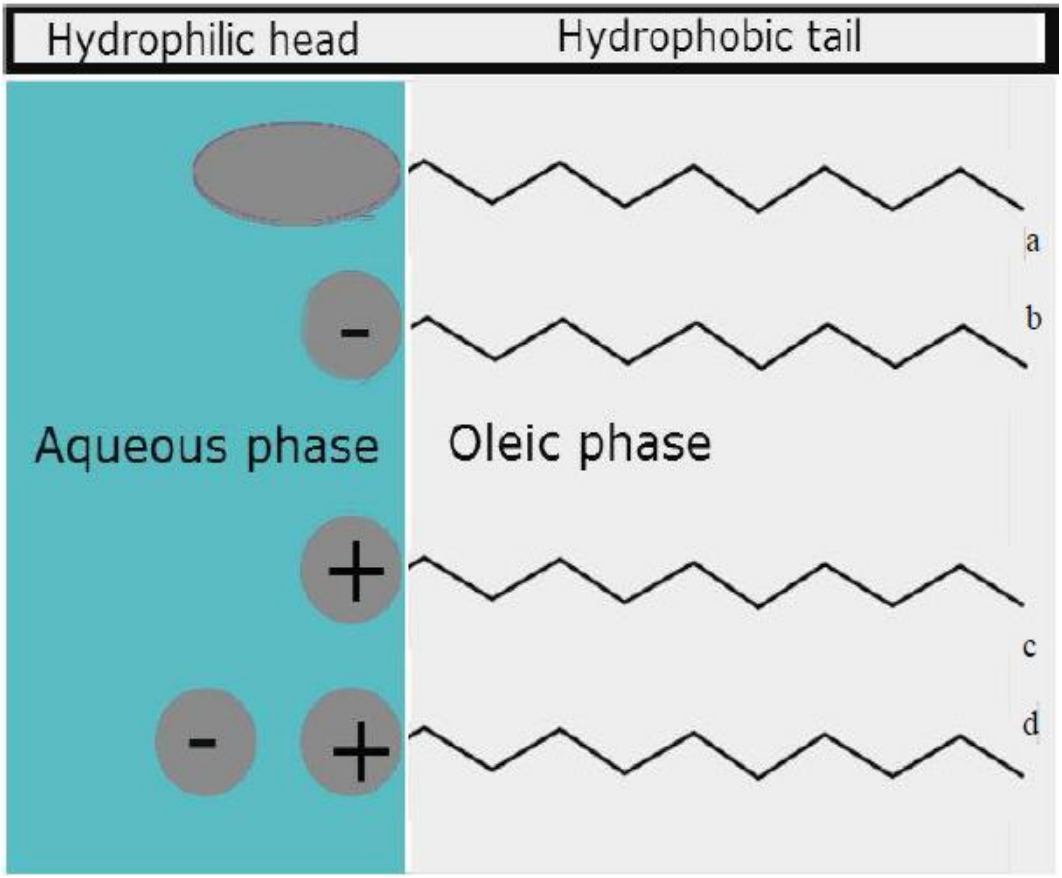


Figure 2-3 Schematic structure of surfactant types (Lange, 2005)
a) Nonionic surfactant b) Anionic surfactant
c) Cationic surfactant d) Zwitterionic surfactant

2.3 FUNDAMENTALS AND PROPERTIES OF FOAM

Foam in porous media is defined as a dispersion of gas in a liquid such that the liquid phase is continuous and at least some part of the gas (in the form of bubbles) is separated by thin films called lamella (Hirasaki, 1989). Surfactant stabilizes the lamella and gas bubbles are separated by these thin films. Thus, the presence of gas, water, and the surfactant is required for foam generation (Rossen, 2013).

Foam can be injected into the reservoirs at least four ways (Rossen, 2013):

1. Co-injection of the gas-surfactant solution. In co-injection, gas and aqueous surfactant solution are injected simultaneously from a single well. Foam forms in the surface facilities where the fluids meet, in the tubing, or shortly after the fluids enter the formation.

2. Alternate injection of gas-surfactant solution. In surfactant-alternating-gas (SAG) injection, gas and surfactant solution are injected separately from a single well. Foam forms in the formation where gas meets previously injected surfactant solution, or when surfactant solution meets previously injected gas.

3. It is possible to dissolve some surfactants directly into supercritical CO_2 (Le *et al*., 2008). Then there is no need to inject aqueous surfactant solution; injected CO_2 with dissolved surfactant forms foam as it meets water in the formation.

4. Injection of gas-surfactant solution from different sections of a vertical well or parallel horizontal wells. In a vertical well, surfactant solution and gas injected simultaneously, but gas injected below the surfactant solution. While injecting gas-surfactant solution from parallel horizontal wells, gas injected from the lower well (Rossen *et al*., 2010; Stone, 2004). This method has not been tested with foam in the field so far.

2.3.1 Introduction to Foam

The concept of using foam was introduced in the 1960s, and it has recently been used in both laboratory and field applications. Foam is not a phase in the reservoir rock because of the separation of gas by thin liquid films (Bernard and Jacobs, 1965). The

behavior of foam in porous media depends highly on the size distribution of the pores and throats, shape and connectivity of the pores (Hirasaki and Lawson, 1985). Figure 2.4 presents the pore-level schematic of foam generated in porous media.

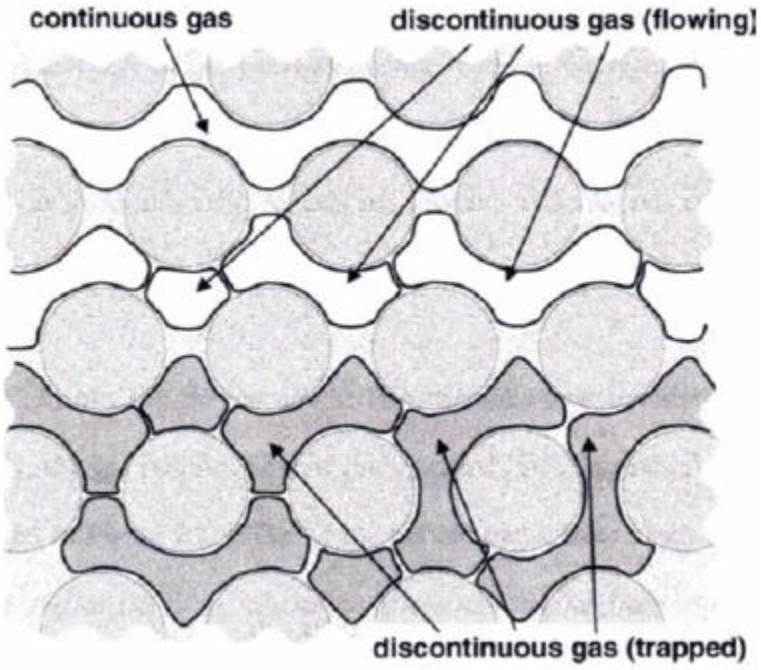


Figure 2-4 Schematic of foam in porous media (Gillis & Radke, 1990)

As shown in Figure 2.4, the gas can be trapped or flowing as a continuous or discontinuous phase. It is important to distinguish continuous and discontinuous gas foams. For regions where lamella cannot be created, a continuous gas phase will form. In continuous gas foam, the porous medium contains some interconnected gas channels. When the gas is continuous, the foam is weak because of the lack of mobility reduction.

Mobility reduction comes from either decrease in relative gas permeability or increase in apparent gas viscosity ($\lambda=k/\mu$). Thus, this continuous gas phase has high mobility due to the high relative permeability and low gas viscosity. In discontinuous gas

foam, the entire gas phase is made discontinuous by lamella and gas channels are not connected (Falls *et al*., 1988). Under co-injection of the gas-surfactant solution, discontinuous gas foam forms. Foam is strong in discontinuous gas foam. Discontinuous gas bubbles face resistance to flow since the lamella makes the flowing gas discontinuous. Strong foam has much greater apparent gas viscosity than weak foam. The combined effect of relative gas permeability and apparent gas viscosity increases the mobility reduction effect of discontinuous gas foam.

Pressure gradient, gas velocity, and pore geometry are the main factors that influence the mobilization or trapping of the foam. Depending on the pressure gradient of the system, the discontinuous gas foam can be trapped or flowing (Bernard and Jacobs, 1965). If the pressure gradient is high enough to displace the lamella from pore throats, the discontinuous gas is flowing. If the pressure gradient is low (or the capillary pressure is too low), gas phase might be trapped. In addition, increasing the pressure gradient can open new channel on the region occupied by trapped gas and discontinuous (trapped) gas can be mobilized (Rossen, 1990).

2.3.2 Foam Generation Mechanism

Liquid lamellae are thermodynamically unstable. This requires constant foam generation for the steady-state presence of foam in porous media. It is generally accepted that there are three major pore-level foam generation mechanisms in porous media: Capillary Snap-off, Lamella Division, and Leave- Behind.

2.3.2.1 Capillary Snap-off

Capillary Snap-off one of the crucial mechanisms for foam generation in porous media. The occurrence of snap-off mainly depends on the ability of the displaced gas to achieve a capillary pressure above the entry pressure (P_e) that allows gas to enter the pore throat (Falls *et al*., 1988). When gas flows from a low into a high permeability zone, snap-off occurs due to reduced capillary pressure (Dicksen *et al*., 2002). Snap-off also depends on liquid saturation, heterogeneity (Ettinger and Radke, 1992), pore geometry, and wettability (Yu and Wardlaw, 1986). Snap-off can occur during multi-phase flow regardless of the presence or absence of surfactant solution. If the discontinuous gas foams are generated by snap-off mechanism and capillary snap-off exists, it is found by Ettinger and Radke that gas mobility can be decreased significantly (1992).

Figure 2.5 provides the mechanism of the capillary snap-off process. As shown in Figure 2.5, a gas finger first enters the pore which is initially filled with liquid. As it passes through the pore throat into the pore body, the leading surface expands. With the expansion of interface, pressure gradient due to the reduced curvature decreases and forces liquid to flow towards pore throat. As liquid accumulates in the pore throat, it finally "snaps off" the flowing gas bubble and separates a single gas bubble into two (or more) gas bubbles while passing through the constriction (Rossen, 1996).

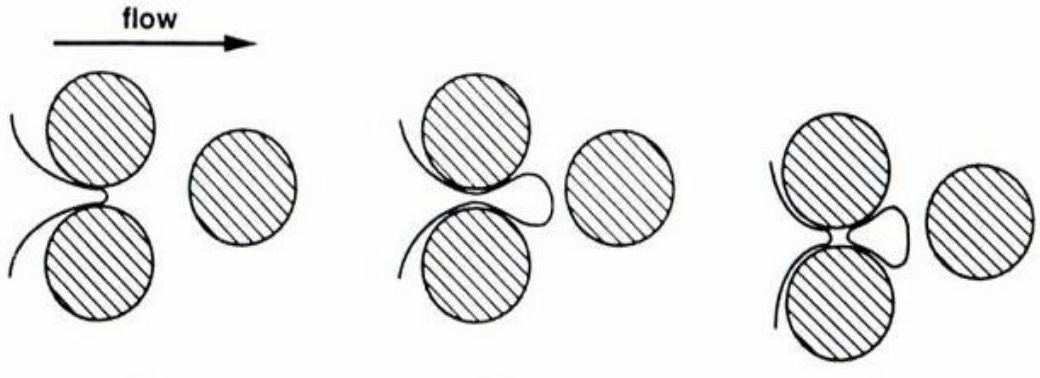


Figure 2-5 Capillary Snap-off Mechanism (Kovscek & Radke, 1994)

2.3.2.2 Lamella Division

The second major mechanism for generation of foam is lamella division. Pressure gradient, bubble size, and pore geometry are the most crucial factors that carry out lamella division mechanism (Yan, 2006). For the existence of lamella division, pressure gradient must exceed a critical value to mobilize the lamellae. One of the requirements for lamella division is that a lamella must pre-exist and be generated by another foam generation mechanism. As indicated in Figure 2.6, a singular flowing gas bubble encounters a branch point, and splits into two lamellae that flow in both directions. The created lamellae that enter both flowing paths are perpendicular to the flow directions. Thus, the number of flowing lamellae is increased, and multiple lamellae create resistance to flow. In addition, moving gas bubble size must be larger than the pore throat so that the lamella span the pore space. Otherwise, gas bubble flow through pore throat without splitting the liquid lamella (Rossen, 2005).

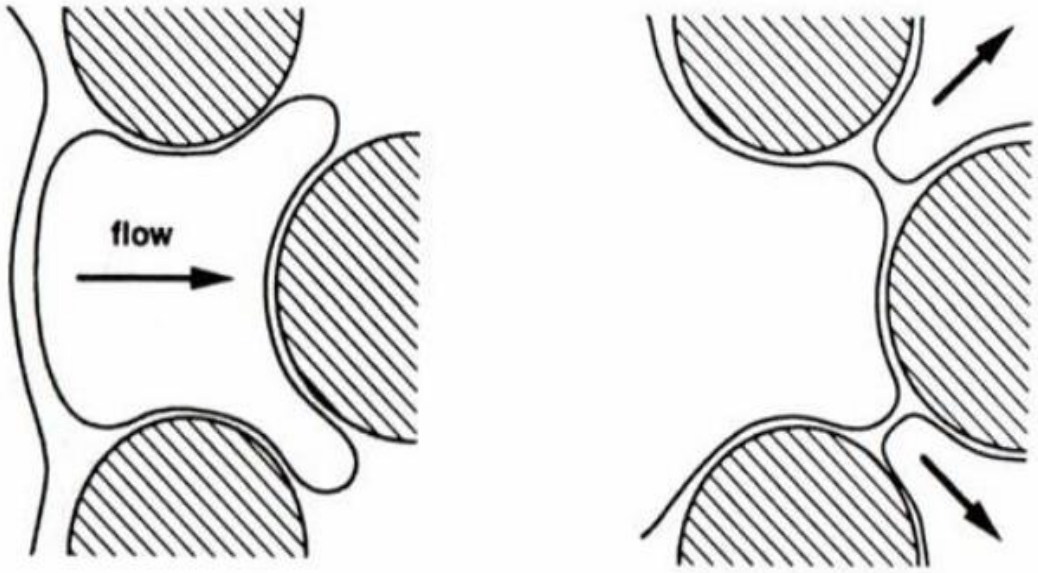


Figure 2-6 Lamella Division Mechanism (Kovscek & Radke, 1994)

2.3.2.3 Leave-Behind

Leave-behind is the third mechanism of foam generation. The process is similar to that in the capillary snap-off mechanism. The difference that there are two gas fingers entering pore throats to create leave-behind lamella. As two gas fingers enter contiguous pore throats and converge at low capillary pressure and pressure gradient during the displacement process, a lamella is then "left-behind" (Owete and Brigham, 1987) as illustrated in Figure 2.7. Since the left-behind lamella is parallel to the flow direction, it does not provide much resistance to flow. Thus, leave-behind mechanism only forms weak foam (continuous gas foam) while capillary snap-off and lamella division can generate discontinuous gas foam, or strong foam.

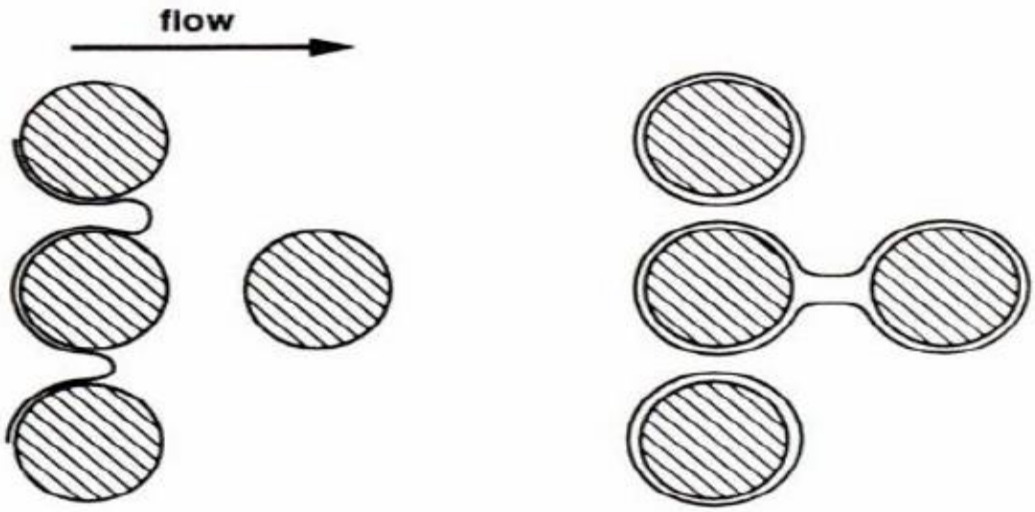


Figure 2-7 Leave-Behind mechanism (Kovscek & Radke, 1994)

2.4 MECHANISMS

Oil recovery processes using chemicals (*e.g.* surfactants) are important EOR methods and are often used to improve the recovery of a wide range of conventional light to heavy oil reservoirs. Residual oil saturation of many reservoirs with respect to water flooding are always economically favorable; however, considerable amounts of oil is remained as trapped which leads to a high residual oil saturation in such reservoirs. Therefore, a tertiary recovery is needed to displace and mobilize residual oil to improve oil recovery.

Wettability is a major factor that controls the location, flow and distribution of fluids in a reservoir (Graue *et al*., 1998). Wettability of the reservoir is critical for the ultimate potential of oil recovery. Water-flooding is an effective technique for fractured reservoirs, if the formation is water-wet. Carbonate reservoirs account for more than 60% of the world's oil and 40% of the world's gas reserves (Andersen *et al*., 2013; Ghosh and Mohanty, 2016; Seethepalli *et al*., 2004). These reservoirs are typically naturally

fractured, highly heterogeneous, and mixed-wet or oil-wet. Recovery from fractured, oil-wet/mixed-wet, carbonate reservoirs by water flooding is typically lower than those from unfractured reservoirs due to the low matrix permeability and oil-wetness. During water flooding, the water preferentially flows through the fractures and does not imbibe into the matrix leading to poor sweep efficiency. Thus, a large volume of the original oil in place remains after water flooding production in these reservoirs. Oil recovery in such reservoirs can be improved by

- Reducing the IFT between oil and water,
- Altering the wetting state of the matrix,
- Increasing the viscous forces
- Providing a better mobility control (Delshad *et al*., 2006)

Extensive studies on carbonate core samples have shown that nearly 85% of these reservoirs tend to be oil-wet or intermediate wet (Andersen *et al*., 2013). In order to displace higher amount of oil from carbonate reservoirs, wettability alteration towards more water-wet condition must be achieved. A key recovery mechanism in such condition is the spontaneous imbibition of water into the rock matrix. Spontaneous imbibition is a process where a wetting phase displaces the non-wetting phase in a porous media by capillary action. When the rock is more oil-wet/mixed-wet, the spontaneous imbibition mechanism is slow and will not lead to substantial recovery. It is important for fractured carbonate reservoirs to produce oil from the rock matrix for a better recovery. Water flooding produces oil from these reservoirs through spontaneous imbibition of water into the rock matrix and the flow of the oil out of matrix through the fractures.

Many literatures have reported the wettability alteration towards water-wetness caused by surfactants. Surfactant solution can be added in the injected fluid, diffuse into the matrix, adsorb on the rock and alter the wettability towards a more water-wet state, depending on the degree of adsorption (Andersen *et al*., 2013). In water-wet reservoirs, the oil typically occupies the larger pore spaces while the water is held/trapped in the much smaller pores and/or pore throats (Kalaei *et al*., 2013).

Surfactant flooding has the potential to improve oil recovery in oil-wet reservoirs by lowering the interfacial tension (IFT) between oil trapped in small capillary pores and the water surrounding those pores, thus mobilizing the oil. Wettability alteration and IFT reduction are the mechanisms that lead to spontaneous imbibition of water and thus, improve oil recovery. The use of surfactant solutions that increase oil recovery has been deeply studied in the literature.

Austad and coworkers have conducted a series of studies on oil-wet carbonate cores using surfactant solutions and observed the effects of surfactant types on oil recovery (Austad and Milter, 1997; Standnes and Austad, 2000; Standnes and Austad, 2003). They have shown that anionic surfactants are quite effective in imbibing water into originally oil-wet cores with the recovery factor of nearly 70% OOIP. They concluded from their studies that most of the tested cationic surfactants resulted in higher adsorption rate on the rock surface. Nonionic surfactants and anionic surfactants have been tested by Chen *et al*. (2000) in both laboratory and field applications. Laboratory experiments indicates that the injection of nonionic surfactants resulted in an improved oil recovery compared to an injection of reservoir brine alone. In 2003, Strand *et al*. identified several

commercial surfactants and observed that these surfactants could recover 50 to 90% of oil from the core samples in laboratory experiments.

Hirasaki and Zhang (2004) used different surfactant solutions to recover oil from dolomite cores. Their work was different from earlier work, because sodium carbonate and anionic surfactants were used to achieve wettability alteration and IFT reduction. Several surfactant and alkali formulations were studied. The wettability was altered because surfactant changes the charge at the calcite/brine interface from positive to negative. Imbibition experiments were also conducted using several surfactant/alkali formulations and additional oil was recovered when the imbibition was enhanced. Shuler *et al*. (2011) studied the performance of anionic and nonionic surfactants in cores with permeabilities from 2 to 10 md. They concluded that adding surfactants to fracturing fluids should increase oil recovery by wettability alteration, however they could not find out which surfactant shows the best performance on the alteration process.

Wang *et al*. (2012) conducted wettability and imbibition experiments on cores to observe the effect of wettability alteration on imbibition process. They concluded that some surfactants altered wettability from oil-wet towards water-wet and imbibed into the cores to displace more oil than brine alone, thereby improving oil recovery. Kathel and Mohanty (2013) studied the effect of anionic and nonionic surfactants in a tight sandstone reservoir with permeabilities from 0.01 to 0.1 md and porosities from 8 to 14%. Wettability was measured by the contact angle method. Contact angle experiments indicated that anionic surfactants altered wettability from oil-wet to water-wet, whereas nonionic surfactants failed in changing wettability. As a result of imbibition experiments

with Amott cells, the authors concluded that surfactants imbibed and recovered more oil than brine alone.

Next, Alvarez *et al*. (2014) studied the wettability alteration of anionic and nonionic surfactants by use of contact angle method on carbonate cores (porosity of 3–5%), and investigated the change in IFT. In addition, they conducted core flooding experiments to observe fluid imbibition into the core samples to simulate a fracture. They concluded that surfactants altered wettability and reduced IFT, and imbibition into the cores was achieved by surfactant flooding and more oil was recovered than brine without surfactants. Nguyen *et al*. (2014) evaluated different surfactants on shale core samples with the variety of porosity range. Spontaneous imbibition results showed that all surfactants improve oil recovery in imbibition experiments, with the anionic surfactant being the most effective. Finally, Morsy and Sheng (2014) studied surfactant performance on shale samples. After stability tests, they concluded from the spontaneous imbibition experiments that higher recovery factor was achieved by use of surfactant than brine alone.

2.5 WETTABILITY

As mentioned above, wettability is a major factor that controls location, flow, and distribution of fluids in porous media (Anderson, 1986). Fluid distributions in porous media are affected by the forces at both fluid/fluid and fluid/solid interfaces. Viscous forces and capillary pressure are the two most important physical phenomena in flow through porous media. Viscous forces are reflected in the magnitude of the pressure drop that occurs due to the flow of a fluid through the medium and can be expressed by

Darcy's Law. The pressure difference between wetting and non-wetting phases is capillary pressure and it can be related to interfacial tension and contact angle (wettability) by Young-Laplace equation. Capillary pressure is caused by curved boundaries between different fluid phases in a pore (Lake, 1989). Pore geometry and surface interaction determine the shape of interface and curvature at a given saturation (Graue *et al*., 1999).

Oil recovery results from a competition between capillary and viscous forces. Chemicals (i.e. surfactants) can be used to increase the viscous forces by changing wettability and thereby improve oil recovery. Pressure head in the non-wetting phase must exceed capillary entry pressure to displace the wetting phase and enter the pore. In carbonate reservoirs, for instance, due to the low permeability and narrow pore throats, capillary forces are dominant and capillary effect is the main reason for a large amount of oil trapped in pores which cannot be recovered by water flooding. Capillary forces can be overcome by reducing interfacial tension to ultra-low values or changing wettability.

2.5.1 Wettability Definition and Classification

Wettability is defined as the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids (Anderson, 1986). Wettability is the result of interaction between fluid (water, oil, gas) and solid (such as rock surface) phases. When two immiscible fluids are in contact with a solid surface, one phase usually attracted to the solid surface more than the other phase. Strongly attracted phase is called wetting phase. Wettability is mainly affected by rock minerology, composition of fluids, and saturation history (Agbalaka *et al*., 2008).

Wettability generally can be classified as either homogeneous or heterogeneous. In a homogeneous system, according to Anderson (1986), if a thin water film prevents contact between the hydrocarbon phase and solid surface, reservoir wettability is **fully water-wet**. The rock matrix is covered by a thin oil film at all times in **fully oil-wet** reservoirs. In **intermediate wet** reservoirs, the oil/water interface makes a distinct contact angle with rock matrix. In a heterogeneous system, the reservoir can be either **fractional-wet** or **mixed-wet**. In fractional wettability, the internal rock surface consists of a distribution of water-wet and oil-wet sections. The reservoir exhibits local areas that are strongly oil-wet while most of the reservoir is fully water-wet. This state occurs when the reservoir rock contains different minerals that adsorb distinct parts of the rock matrix and minerals may have different wetting characteristics. The rock is called mixed wet if the larger pores are filled with oil and become oil-wet whereas the smaller pores are filled with water and remain water-wet. Low residual oil saturation exists in a mixed-wet system.

2.5.2 Wettability Measurements

2.5.2.1 Contact Angle

The contact angle measurement is the most widely-used method for measuring the reservoir rock wetting state. For a single-phase fluid in contact with a solid surface, the contact angle is the angle between fluid-solid interface. When two immiscible fluids (i.e. oil and water) are together in contact with rock surface, the contact angle is defined by the angle measured through the water droplet on the solid surface (Agbalaka *et al*., 2008) as shown in Figure 2.8. Dynamic Wilhelmy method, static and dynamic sessile drop methods have been used commonly to measure contact angle.

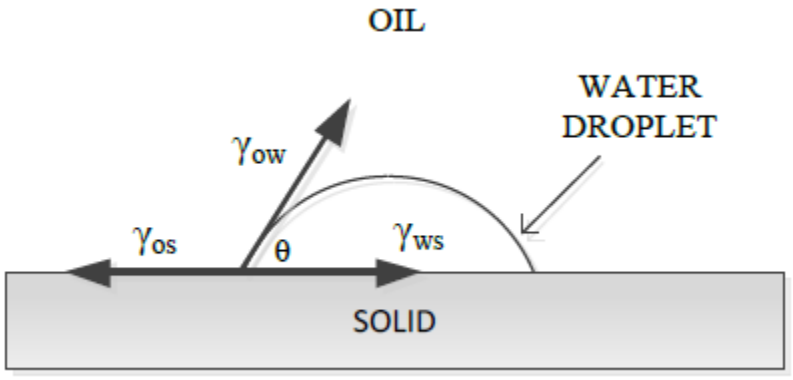


Figure 2-8 Contact angle of a water droplet on a solid surface

Contact angle in oil/water/rock system defines which fluid wets the rock surface. It is usually measured through the denser liquid (water) phase. The relationship between the surface energies in Figure 2.8 and the contact angle are defined by Young's equation:

$$\gamma_{ow}cos\theta = \gamma_{os} - \gamma_{ws}$$

If reservoir wetting condition is defined in terms of contact angle, then when $0^o<\theta<75^o$, the reservoir rock is preferentially water-wet. In the range of $75^o<\theta<115^o$, it is defined as intermediate wet. When it is $115^o<\theta<180^o$, the system is preferentially oil-wet (Figure 2.9).

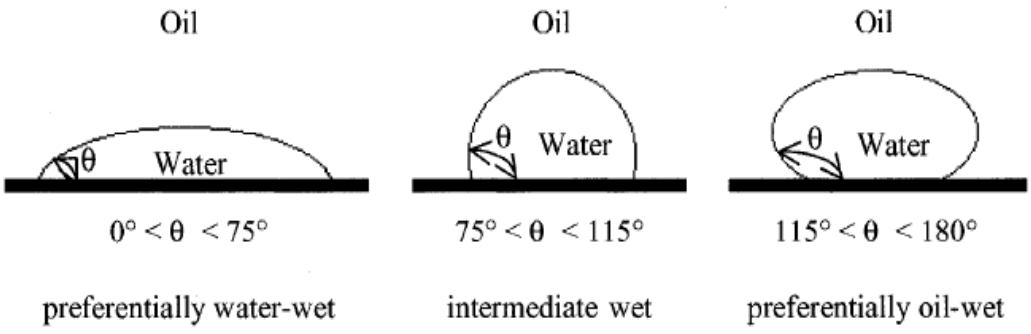


Figure 2-9 Wettability definition with contact angle (Morrow, 1990)

2.5.2.2 Amott Wettability Measurement

The Amott wettability is a macroscopic average wettability measurement for a solid/fluid system. In includes measuring both forced and spontaneous imbibition amounts for a reservoir rock sample. Amott wettability can be calculated according to following equation:

$$WI_{AMOTT} = I_w - I_o$$

Amott wettability index (WI_{AMOTT}) reflects the ease with which the wetting phase will displace the non-wetting phase (spontaneous imbibition). For strongly water-wet systems, oil index (I_o) will be zero which indicates that oil is not imbibed spontaneously. Similarly, water index (I_w) will be zero for strongly oil-wet systems (Agbalaka *et al*., 2008). Amott wettability index neglects the hysteresis of capillary pressure curve and this method is used as a standard measurement for comparing the wettability of different core samples.

2.5.2.3 USBM Method

USBM wettability is calculated according to following equation and this method is also a macroscopic average wettability measurement for a solid/fluid system.

$$WI_{USBM} = log(\frac{A_w}{A_o})$$

For extremely water-wet systems, USBM wettability index (WI_{USBM}) is very large and positive while it is very large and negative for extremely oil-wet systems. For an intermediate wet condition, WI_{USBM} lies around zero (Agbalaka *et al*., 2008). Unlike Amott Wettability, USBM method considers the hysteresis effect of capillary pressure.

2.6 DISPLACEMENT MECHANISM OF SURFACTANT-GAS FLOODING

Surfactant-gas flooding has long been demonstrated to be a prospective enhanced recovery method in oil industry. There are some mechanisms that are associated with displacement during surfactant-gas flooding, but the main effects that surfactant-gas flooding depends on are wettability alteration, reduction of interfacial tension, spontaneous imbibition, as well as foam generation and its mobility control.

2.6.1 Wettability Alteration

Wettability of the matrix rock is an important characteristic that defines whether the water will be sucked into the rock (water-wet) or simply flow around (oil-wet). Wettability plays a significant role in oil recovery process. Studies have confirmed that wettability alteration directly affects the recovery from a reservoir. As mentioned above, surfactants have been used to alter the wettability to enhance oil recovery by increased imbibition of the water into the matrix rock. The surfactant molecules diffuse/flow from fractures into the rock matrix and alter the wettability of the rock in naturally fractured reservoirs (Gupta and Mohanty, 2008). Wettability alteration results in strong reduction in the residual oil saturation.

Hydrocarbon recovery results from a competition between capillary and viscous forces. In most carbonate reservoirs, spontaneous imbibition is the major recovery mechanism. The dominance of capillary forces is due to narrow pore throats, more or less water wet conditions and the low permeability of this rock (Graue *et al*., 1998). Capillary pressure (P_c) can be written as:

$$P_c = \frac{2\sigma cos\theta}{r},$$

where σ is oil-water IFT, θ is the contact angle, and r is the capillary pore radius.

Many authors studied the effect of wettability on capillary pressure and relative permeability. When wettability is changed by use of surfactant solutions, capillary pressure and relative permeabilities change wherever the surfactant contacted to the rock surface (Kalaei *et al*., 2013). The surfactant molecules diffuse/flow from fractures into the matrix and change wettability and IFT. In general, relative permeability of phase *j* can be expressed as

$$k_{rj} = k_{rj}^{o}(\frac{S_j - S_{rj}}{1 - \sum S_{rj}})^{n_j},$$

where k_{rj}^{o} is the endpoint relative permeability of phase *j*, S_j is the saturation of phase *j*, S_{rj} is the residual saturation of phase *j*, and n_j is the exponent of phase *j*. Matrix curves for relative permeabilities defined for initially oil-wet system are given in Figure 2.10 (Lashgari *et al*., 2016). As shown in the figure, the effect of wettability alteration is similar to IFT reduction. The IFT reduction causes differences in the final state such that residual saturations become zero, the endpoint relative permeability increases to one, and relative permeability exponent decreases to one. On the other hand, in wettability alteration, increase in residual water saturation and decrease in residual oil saturation can be observed between initial and final states. Moreover, note from the relative permeability curves that the oil endpoint relative permeability increases while the water

relative permeability endpoint decreases. In addition, water exponent increases while the oil relative permeability exponent tends toward to one.

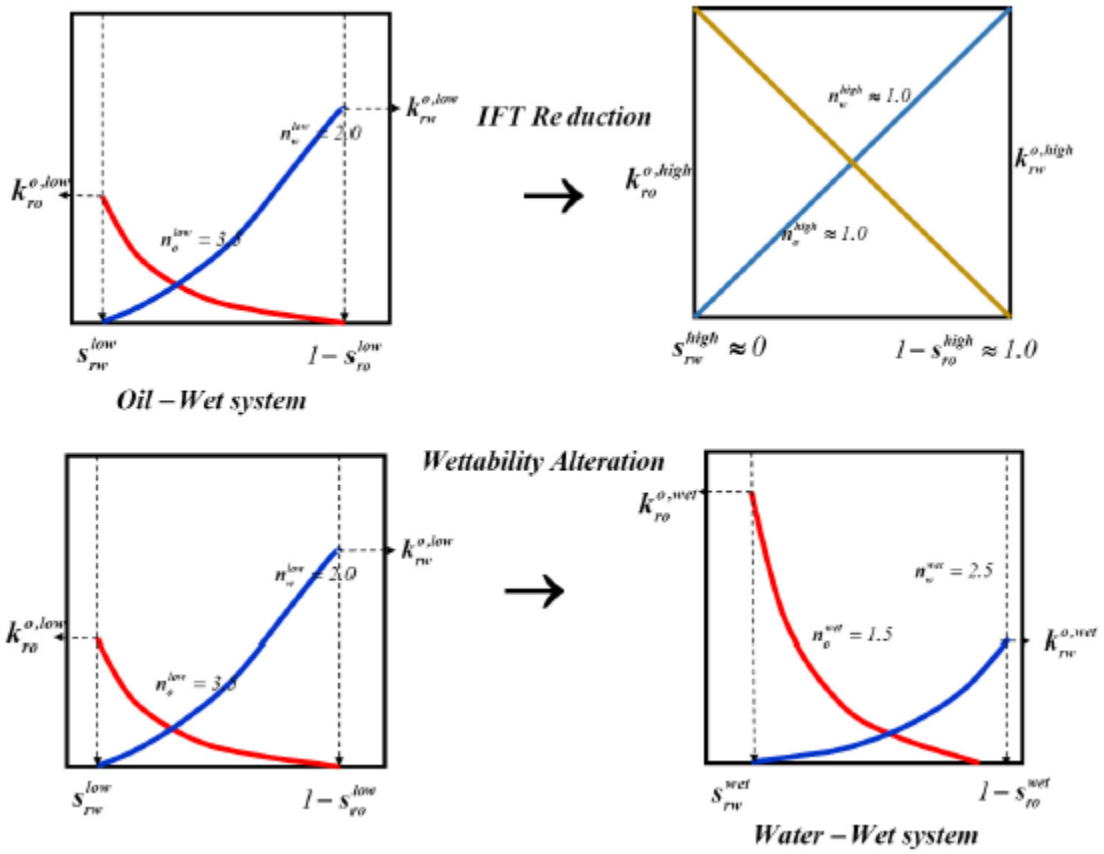


Figure 2-10 Shematic of relative permeability parameter changes due to IFT reduction and wettability alteration

Trapping number (N_T) can reasonably model the combined effects of viscous, capillary, and gravitational forces (Lashgari *et al*. 2016). Trapping number of phase *j* can be computed from the following equation:

$$N_{Tj} = \frac{-\vec{k}.(\vec{\nabla}(P_D - P_{cdD}) + g(\rho_d - \rho_D)\vec{\nabla}\mathrm{h})}{\sigma_{dD}},$$

where d and D are the displaced and displacing fluids, respectively. P_D is the flow pressure of the displacing phase and P_{cdD} is the capillary pressure between the two displacing and displaced phases, g is the gravitational acceleration; $\vec{k}$ is the permeability tensor; h is the height with respect to a reference datum; ρ_d and ρ_D are densities of the displaced and displacing fluids, respectively. σ_{dD} is the IFT between displacing and displaced phases.

Lashgari *et al*. (2016) also evaluate the effect of wettability on relative permeabilities of water and oil with the range of low to high trapping numbers considering various contact angles. Figure 2.11 illustrates oil and water relative permeability curves while the wettability state changes from oil wet towards more water wet conditions. It can be concluded from these figures that wettability alteration has a significant effect on the fluid flow at lower trapping numbers.

At a low trapping number, an additional comparison was made by Lashgari *et al*. (2016) to observe the effect of wettability on capillary pressure in different contact angles. Results supported by Figure 2.12 showed that spontaneous imbibition of water into the matrix cannot occur while capillary pressures are high (corresponds to oil-wet state). However, altering wettability towards more water-wet states results in the spontaneous imbibition of water, thus drive oil from fractures to the rock matrix.

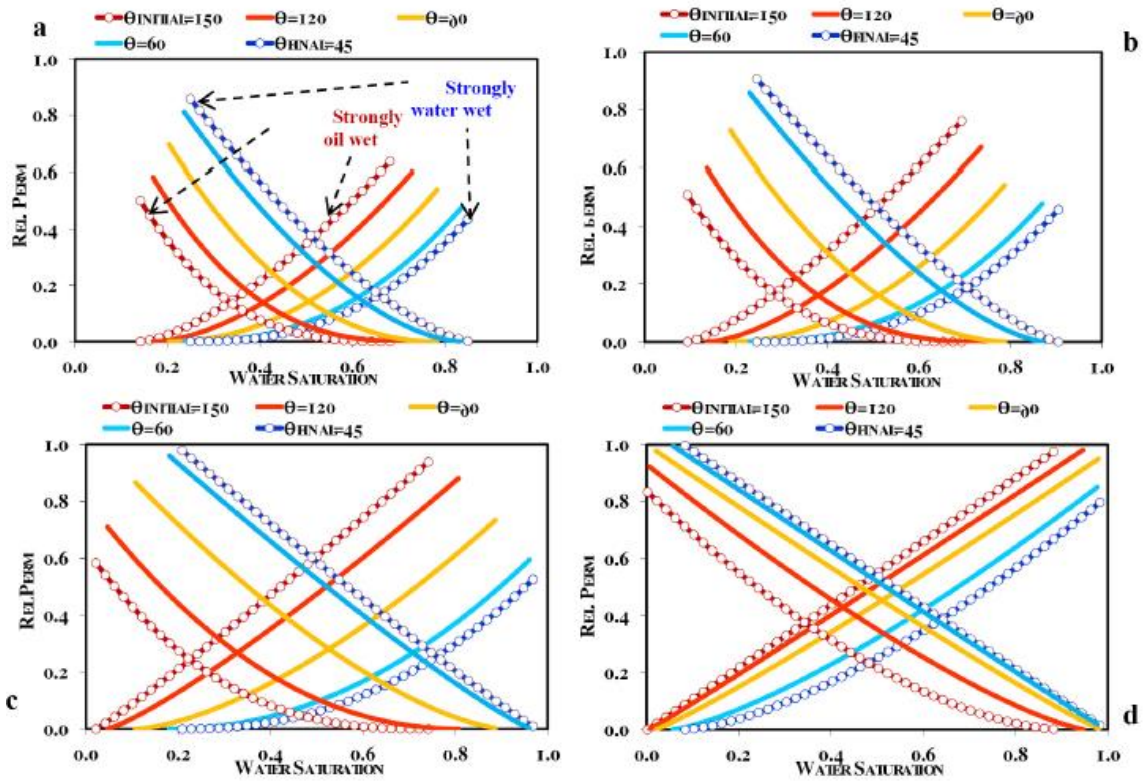


Figure 2-11 **The effect of wettability considering various contact angles on oil and water relative permeabilities**

(a) low trapping number N_T_1.0E-6, (b) N_T_1.0E-5, (c) N_T_1.0E-4, and (d) high trapping number N_T_1.0E-3.

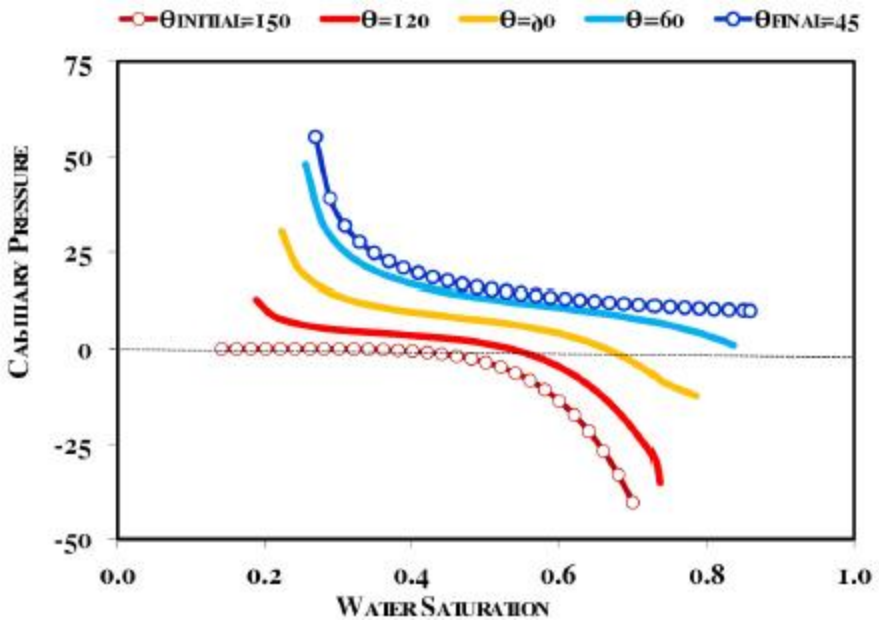


Figure 2-12 Effect of wettability considering various contact angles on capillary pressure at a low trapping number (*N_T_1.0E-6)*

2.6.2 Interfacial Tension Reduction

There is a tension between any two phases due to the dissimilarity of the intermolecular forces between the molecules. These molecular interactions create a force that tends to contract the interface to a smaller area which creates a tension which is interfacial tension. In addition to wettability alteration, oil recovery can be improved by decreasing the interfacial tension between the oil and water. It is well-known that surfactant has the potential to improve oil recovery in fractured carbonate reservoirs by reducing the interfacial tension to ultra-low values between oil trapped in small capillary pores and the water surrounding those pores, thus mobilizing the oil. Capillary forces are proportional to the interfacial tension between oil and displacing phase, so the trapped oil can be mobilized by using miscible fluids or a significant decrease in IFT between the

displacing phase and the trapped oil. Reduction in oil-water interfacial tension decreases capillary entry pressure and thus push the trapped oil in small pores. Viscous forces overcome the entry capillary pressure, water invades the matrix, pushes the oil from small pores to the fractures, and thereby improving oil recovery (Gupta and Mohanty, 2008; Kalaei *et al*., 2013; Lashgari, 2016).

2.6.3 Spontaneous Imbibition

Spontaneous imbibition is a process where a wetting phase displaces the non-wetting phase in a porous media by capillary action (Yu *et al*., 2008). Spontaneous imbibition rate is a function of matrix permeability (Mattax and Kyte, 1962), wettability (Morrow *et al*., 1994), interfacial tension and curvature of the interface (Hatiboglu and Babadagli, 2007), shape and size of the matrix (Olafuyi *et al*., 2007).

In strongly water-wet conditions, the primary driving force for spontaneous imbibition is capillary forces. For systems that are preferentially oil-wet, spontaneous imbibition would not occur due to capillary force that retains oil in the matrix. Water flood performance is poor in such reservoirs because of the tendency of injected water flowing in the fractures. Thus, sweep efficiency is not very sufficient. The introduction of surfactant solution will improve oil recovery by both wettability alteration and interfacial tension reduction. In naturally fractured oil-wet reservoirs, due to the reduced interfacial tension, oil tends to leave the matrix since surfactant solution overcomes the capillary forces and change the capillary pressure from negative to positive value which then leads to spontaneous imbibition. Water flooding produces oil from these reservoirs

through spontaneous imbibition of water from the fractures into the rock matrix and drives oil out of the matrix through the fractures. In most carbonate reservoirs, spontaneous imbibition is the main recovery mechanism.

2.6.4 Foam for Mobility Control

As defined before, foam is dispersion of gas in a liquid that the liquid phase is continuous or connected, and at least some parts of the gas is discontinuous by thin liquid films (lamellae). Foams have been widely used as mobility control agents for channels, fractures, or high permeability layers since they have potential in improving oil recovery.

Since gas has low viscosity and low density, it is difficult to achieve a good sweep efficiency during gas flooding. The use of foams has advantage for a better volumetric sweep efficiency when compared to the use of gas only. Because, foam lowers the gas mobility in the swept or higher permeability regions of the reservoir. The reduced mobility comes from the reduction in gas relative permeability as well as rise in apparent viscosity. Stationary lamellae trap the gas and trapped gas in some pore space blocks gas pathway which reduces the relative gas permeability (Schramm, 1992). In addition, moving lamellae cause a resistance to gas flow due to the rise in apparent gas viscosity that leads to reduction in gas mobility and provide better volumetric sweep (Falls *et al*., 1989). The combined effect of the reduction in gas relative permeability and the increase in apparent gas viscosity greatly increases the mobility reduction effect of foam during EOR processes.

Instead of using just surfactant solutions as displacement agents, the use of foam can recover more oil and provide better sweep efficiency in carbonate reservoirs. The efficiency of the foam is believed to be the result of the high foam viscosity (apparent viscosity) and its penetration into the fractures. Application of foam in porous media requires foam generation. Foam can be generated by co-injection or alternate injection of gas and foaming agent (surfactant). Mobility control is the major mechanism in foam assisted flooding and it can be achieved by the considerable reduction of gas mobility in the foamed region. This lowered gas mobility diverts at least some of the displacing phase into the other parts of the formation that were previously un-swept, thereby additional oil is recovered.

Foam flooding was introduced in the 1960s, and has recently become actively used in both laboratory experiments and field applications. Use of foam as a mobility control agent was first proposed by Lawson and Reisberg (1980). They studied alternate injection of an inert gas and surfactant solution for providing mobility control in chemical flooding. In their experiments, chemical slug was displaced by alternate injection of gas and surfactant. They observed that as long as gravity segregation and foam drainage is prevented, foam generation achieves greater performance on improving oil recovery than polymer flooding.

The first ultra-low interfacial tension field test was achieved by Wang and coworkers (Wang *et al*., 2001). Then, they conducted series of laboratory experiments on sand packs with the co-injection of surfactant slug and gas in 2006. They observed that the co-injection of surfactant slug and gas is more effective when the oil saturation is low. This

is because foam is more stable at low oil saturations. They found that foam drive process is more effective when alkali is added in the slug. Addition of alkali leads to ultra-low IFT conditions without adding extra surfactant and reduces surfactant adsorption. Compared to water-wet flowing conditions, oil-wet conditions reduce the effects of flowing foam, thus results in poor oil recovery.

Li *et al*. (2008) studied nitrogen foam flooding efficiencies at Shengli oilfield. They conducted experiments, performed numerical simulation and field tests to optimize the conditions and develop a reservoir-condition screening criterion. They concluded from their study that this process has stronger blocking ability due to the reduction in the mobility of gas. Furthermore, nitrogen foam blocks the channels, and restricts the flow of displacing phase in high permeability zones. They concluded that this technique is more effective for heterogeneous formations. In addition, Li and coworkers tested mobility control in sand packs by the alternate injection of surfactant and gas. Anionic surfactants were used in the process, good foaming ability was achieved in the drive, and mobility control was provided by foam. Almost piston like oil displacement was observed in the experiments (Li *et al*., 2008).

Le *et al*. (2008) performed a series of experiments on carbonate rocks to study the injection strategy for foam generation. They applied several injection strategies, including SAG (surfactant-alternating-gas), WAG (water-alternating-gas with surfactant injected in CO_2), and continuous CO_2 injection with dissolved surfactant. The foam was generated in all injection strategies. Moreover, CO_2 injection with dissolved surfactant greatly reduced gas mobility compared to the other strategies, which indicated foam performance as

mobility control agent. Farajzadeh *et al*. (2009) reported an experimental study of CO_2 and N_2 foam flows in sandstone cores. They partially saturated the cores with oil and brine, and brine only. The CO_2 and foaming agent (surfactant) were injected to the cores. They observed increasing oil recovery when surfactant injection followed by CO_2 injection. The presence of oil does not allow the generation of foam in the porous medium. In addition, they concluded that it is possible to reduce the mobility of CO_2 when there is no oil present. Moreover, they found that N_2 can form weak foam zone in the presence of oil.

Haugen *et al*. (2012) studied N_2 foam flow in fractured, oil-wet limestone rocks. They performed several experiments on foam flow in fractured cores where the fractures are in contact with a porous matrix. The maximum oil recovery was obtained when large numbers of pore volume were injected. Simjoo *et al*. (2012) investigated the effects of oil on foam stability and oil recovery. Foam was generated by co-injecting nitrogen gas and surfactant. Two main oil recovery regimes were observed. The first oil recovery arises from the formation of an oil bank, while the second regime corresponds to oil displacement as a dispersed phase that is transported by foam lamellae. Moreover, higher mobility reduction and improved oil recovery were achieved subject to the injection of foam. Hou *et al*. (2012) have conducted laboratory experiments on highly heterogeneous conglomerate rocks. They applied nitrogen foam formulas to the core samples and concluded that the direct injection of foam is better than the co-injection of gas and surfactant solution.

Chapter 3: SUMMARY and CONCLUSIONS

In this chapter, we summarize our finding based on the literature review in this work and conclude the insights of this report.

3.1 SUMMARY

Oil recovery can be divided into three categories: primary, secondary, and Enhanced Oil Recovery. Primary recovery is driven by using natural reservoir energy and artificial lift techniques. Secondary production refers to the injection of water or/and gas for pressure maintenance to drive oil from the reservoir. Water flooding is the main secondary recovery technique to maintain enough reservoir pressure to drive oil after primary production. However, it is not effective in naturally fractured carbonate reservoirs because water flows preferentially in the fractures and negative capillary pressure keeps water from entering the matrix, leading to a high residual oil. It is estimated that a recovery of 35-50 % original oil in place (OOIP) can be achieved by combined primary and secondary production and high amount of residual oil is left behind after these techniques.

There are three major factors that affect the remaining oil saturation in a reservoir. The first factor is the capillary number. It affects the microscopic pore-level displacement efficiency. The second factor is the mobility ratio. It influences the volumetric displacement efficiency. At large mobility ratio, displacing fluid tends to bypass oil, resulting in poor oil recovery. High sweep efficiency can be achieved when mobility ratio is less than one ($M < 1$), but small mobility ratio means low injection rate. Thus, a

practical mobility ratio is a compromise between mobility control and injection rate. Mobility can be controlled by adding polymer and foam. Reservoir heterogeneity is the third major factor that can influence the residual oil saturation. Reservoirs can contain impermeable layers and heterogeneous porosity/permeability distributions that notably affect the fluid flow path and distribution.

How can the microscopic displacement efficiency be improved? Residual oil remains trapped in the reservoir and it can be mobilized by using miscible fluids or reducing the interfacial tension between the displacing fluid and the trapped oil to ultra-low values reservoir heterogeneities, gravity segregation and viscous fingering are the main reasons for poor volumetric sweep efficiency. In order to achieve an effective sweep, it is possible to change the mobility ratio by either decreasing the mobility of the displacing fluid or by increasing the mobility of the displaced oil.

Thermal methods are important recovery processes in heavy oil reservoirs and include steam flooding, hot-water injection, in-situ combustion, and electrical heating. Thermal processes rely mainly on the injection of thermal energy or the in-situ generation of heat to improve oil recovery. Alteration of oil viscosity and achievement of favorable conditions such as thermal expansion or swelling of the oil are the primary mechanisms leading to improved oil recovery in thermal methods. Gas injection is another recovery method where the recovery efficiency significantly depends on the miscibility. Availability of sufficient gas supply is the most common limitation for the miscible gas injection method. Chemical injection is an effective method in reducing residual oil saturation and it is considered as a promising EOR application in many fields. In

chemical flooding, chemicals are added to achieve: wettability alteration, IFT reduction, and mobility control. A promising cost-effective chemical EOR process is to combine surfactant flooding with gas injection to generate foam. This method provides better mobility control. Foam can be generated by co-injection or alternate injection of gas and foaming agent (surfactant). Mobility control is obtained in the foamed region since the permeability of gas in the foamed region is reduced significantly. Foam can penetrate into the high permeability layers and/or fractures and recover more oil by achieving efficient volumetric sweep. Recovery mechanisms in foam flooding are: Reducing interfacial forces that hold residual oil in place, and the capability of altering flow distribution. As a result, it is important to understand foam performance in a foam assisted surfactant-gas flooding process.

3.2 CONCLUSIONS

The following conclusions are obtained from this study:

- Anionic surfactants can change the wettability to intermediate/water-wet condition as well as or better than the cationic surfactants.
- Anionic surfactants have low adsorption on the rock matrix. They are relatively stable and have a low cost on EOR processes.
- Due to the high adsorption rate on the rock surface, cationic surfactants are rarely used in EOR applications. These surfactants are generally more expensive than anionic surfactants.
- The presence of gas, water, and the surfactant is required for foam generation.

- Pressure gradient, gas velocity, and pore geometry are the main factors that influence the mobilization or trapping of the foam
- Oil recovery results from a competition between capillary and viscous forces and the use of surfactants increases the viscous forces by changing wettability and thereby improve oil recovery.
- Wettability alteration directly affects the recovery from a reservoir. Surfactants alter the wettability to enhance oil recovery by increased imbibition of the water into the matrix rock.
- Surfactant has the potential to improve oil recovery in fractured carbonate reservoirs by reducing the interfacial tension to ultra-low values between oil trapped in small capillary pores and the water surrounding those pores.
- Reduction in oil-water IFT decreases capillary entry pressure and thus push the trapped oil in small pores. Viscous forces overcome the entry capillary pressure, water invades the matrix, pushes the oil from small pores to the fractures, and thereby improving oil recovery.
- Spontaneous imbibition rate is a function of matrix permeability, wettability, interfacial tension & curvature of the interface, shape and size of the matrix.
- For preferentially oil-wet reservoirs, spontaneous imbibition would not occur due to capillary force that retains oil in the matrix. Water flood performance is poor in such reservoirs because of the tendency of injected water flowing in the fractures.

- The introduction of surfactant solution will improve oil recovery by both wettability alteration and interfacial tension reduction. In naturally fractured oil-wet reservoirs, due to the reduced interfacial tension, oil tends to leave the matrix since surfactant solution overcomes the capillary forces and change the capillary pressure from negative to positive value which then leads to spontaneous imbibition. Spontaneous imbibition is the main recovery mechanism in most carbonate reservoirs.
- Since gas has low viscosity and low density, it is difficult to achieve a good sweep efficiency during gas flooding. The use of foams has advantage for a better volumetric sweep efficiency due to the reduced gas mobility in the swept or higher permeability regions of the reservoir when compared to the use of gas only.
- The combined effect of the reduction in gas relative permeability and the increase in apparent gas viscosity greatly increases the mobility reduction effect of foam during EOR processes.
- Recovery from fractured, oil-wet/mixed-wet, carbonate reservoirs by water flooding is typically lower than those from unfractured reservoirs due to the low matrix permeability and oil-wetness. During water flooding, the water preferentially flows through the fractures and does not imbibe into the matrix leading to poor sweep efficiency. Thus, a large volume of the original oil in place remains after water flooding production in these reservoirs.

- Reduction in IFT between oil and water, alteration of wettability, increasing the viscous forces, and providing a better mobility control by foam are the main mechanisms to improve oil recovery in naturally fractured oil-wet reservoirs.
- Nearly 85% of carbonate reservoirs tend to be oil-wet or intermediate wet.
- The use of surfactant in spontaneous-imbibition experiments accelerates oil recovery and higher recovery factor was achieved by the use of surfactant than brine alone.
- Instead of using just surfactant solutions as displacement agents, the use of foam can recover more oil and provide better sweep efficiency in carbonate reservoirs.
- As long as gravity segregation and foam drainage are prevented, foam generation achieves greater performance on improving oil recovery than polymer flooding.
- The IFT reduction causes differences in the final state such that residual saturations become zero, the endpoint relative permeability increases to one, and relative permeability exponent decreases to one.
- During wettability alteration of water-wet system, increase in residual water saturation and decrease in residual oil saturation observed. Moreover, from the relative permeability curves, the oil endpoint relative permeability increases while the water relative permeability endpoint decreases. In addition, water exponent increases while the oil relative permeability exponent tends toward to one.
- Trapping number (N_T) can reasonably model the combined effects of viscous, capillary, and gravitational forces. Wettability alteration has a significant effect on the fluid flow at lower trapping numbers.

- At a low trapping number, spontaneous imbibition of water into the matrix cannot occur while capillary pressures are high (corresponds to oil-wet state). However, altering wettability towards more water-wet states results in the spontaneous imbibition of water, thus drive oil from fractures to the rock matrix.

Well understanding of chemical and gas EOR methods are reasonably complicated. This report provides a general overview of the literature in foam assisted surfactant-gas flooding. The main limitation of foam field application is the complexity of its flow behavior in porous media. Therefore, more research in this area is strongly recommended to understand its behavior in porous media for the widespread use of conventional foams in oilfields to enhance oil recovery.

NOMENCLATURE

ASP	Alkali/Surfactant/Polymer
EOR	Enhanced Oil Recovery
IFT	Interfacial Tension
M	Mobility Ratio
OOIP	Original Oil in Place
SAG	Surfactant-Alternating-Gas
WAG	Water-Alternating-Gas
E	Overall Displacement Efficiency
E_D	Microscopic Displacement Efficiency
E_v	Volumetric Displacement Efficiency
S_{oi}	Initial Oil Saturation
S_{or}	Residual Oil Saturation
N_c	Capillary Number
v	Superficial Velocity
μ	Fluid Viscosity
σ	Interfacial Tension
θ	Contact Angle
λ_D	Mobility of Displacing Fluid
λ_d	Mobility of Displaced Fluid
k_{rd}	Relative Permeability of Displaced Fluid
μ_d	Viscosity of Displaced Fluid

WI_{AMOTT}	Amott Wettability Index
I_o	Oil Index
I_w	Water Index
WI_{USBM}	USBM Wettability Index
P_c	Capillary Pressure
P_e	Entry Pressure
P_D	Flow Pressure of Displacing Phase
P_{cdD}	Capillary Pressure Between Displacing and Displaced Phases
r	Capillary Pore Radius
k_{rj}^o	Endpoint Relative Permeability of Phase *j*
S_j	Saturation of Phase *j*
S_{rj}	Residual Saturation of Phase *j*
n_j	Exponent of Phase *j*
N_T	Trapping Number
N_{Tj}	Trapping Number of Phase *j*
g	Gravitational Acceleration
$\vec{k}$	Permeability Tensor
h	Height with respect to a reference datum
ρ_d	Density of Displaced Fluid
ρ_D	Density of Displacing Fluid
σ_{dD}	IFT between Displacing and Displaced Phases

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